BOS Slag: Formation, Reaction, and Energy and Materials Recovery

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Abstract: This paper summarises some BOS slag-related researches carried out by the authors. This includes (1) slag formation (i.e. dissolution of lime in the BOS slag), (2) real time *in-situ* observation of high temperature behaviour of synthetic BOS slags, (3) transient phenomena in BOS slags due to metal droplet-slag reactions, and (4) a novel approach to recover energy and materials from molten BOS slags.

I. INTRODUCTION

Basic Oxygen Steelmaking (BOS) process produced over 70% of the world crude steel in 2018, generating 100 to 150 kg of BOS slag for every tonne of crude steel produced. BOS slag, a product of hot metal element (Si, Mn, Fe) oxidation and lime/dolomite dissolution, plays a critical role in the production of high quality crude steel while its behaviour inside the BOS vessel (formation and reaction) is still not clear and its recycling has always been challenging. This paper introduces some BOS slag related research and development performed by the authors, covering the topics of slag formation (lime dissolution), high temperature behaviour by *in-situ* observation, slag-metal droplet reaction mechanisms (spontaneous emulsification), and recovery of energy and materials in the molten BOS slag.

II. LIME DISSOLUTION IN BOS SLAGS UNDER VARYING DYNAMIC CONDITIONS

Quick formation of a suitable slag in BOS process, depending on the fast dissolution of lime in the slag, could increase the process productivity and improve the steel quality at reduced cost. The dissolution behaviour of lime under varying dynamic conditions was studied from a laboratory induction furnace, through a 6t pilot plant converter, to a 320t industry converter [1]. The lime-BOS slag interface under varying conditions (dissolution time, dynamic condition) was characterised by using scanning electron microscopy with EDS (SEM-EDS). It was revealed that the dicalcium silicate (C_2S) layer, which is well reported to exist at the lime-slag interface from laboratory research, was not detected under dynamic conditions. This indicates the boundary layer that would contain C_2S surrounding a lime particle is in fact disturbed through "motion" with the slag in the 6t and 320t converters.

The dissolution of lime in the BOS slags can be described by the two-direction diffusion mechanism (Fig. 1a): outward diffusion of Ca^{2+} and inward diffusion of slag components. The inward diffusion is led by the faster diffusion of the ions of Fe^{2+}, Mn^{2+} and Mg^{2+} (forming a FeO/MnO/MgO-rich layer) and followed by the slower diffusion of anion complexes (forming a C_2S-C_3P solid solution layer).

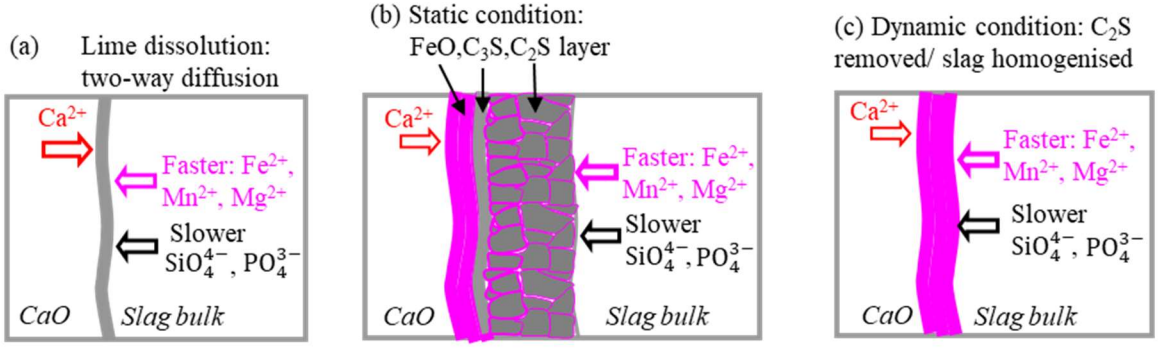

Fig. 1 Schematic diagram showing the mechanisms of lime dissolution in the slags under varying dynamic conditions.

Under static condition (Fig. 1b), a dense and continuous C_2S-C_3P layer is formed next to the bulk

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slag, while a FeO/MnO-rich layer next to lime, and a possible C_3S in between. Under dynamic condition (in the 6t and 320t converters) (Fig. 1c), the boundary layer surrounding the "moving" lime particle with the possibility of the formation of C_2S layer is removed away and slag is homogenised. Therefore, no continuous C_2S-C_3P layer was observed for the slag samples taken from the 6t and 320tconverters).

III. REAL TIME *IN-SITU* DIFFRACTION STUDY ON HIGH TEMPERATURE BEHAVIOUR OF SYSTHETIC BOS SLAGS

One of the key challenges in the BOS process is to efficiently remove the impurity elements from hot metal to BOS slag. Therefore, it is of great importance to study the high temperature behaviour of BOS slag. Various studies have been carried out for the naturally-cooled and or "quenched" slag samples taken from the industrial steelmaking processes and or laboratory experiments. However, with these methods it is not possible to determine if certain phases present in the samples exist at the steelmaking temperatures or form only upon sample cooling. High temperature behaviour of BOS slags is often thermodynamically predicted by using either commercially available packages and or in-house developments. The simulation result is rarely validated due to the lacking of high temperature experimental results of the multi-component slags.The high temperature behaviour of synthetic BOS slags (up to 1700 °C) was studied by developing a real time *in-situ* neutron diffraction method on GEM at ISIS facility (UK) [2]. Data analysis of the collected neutron diffraction data yielded relative phase fractions and structure parameters of the phases present in the slag samples as a function of composition and temperature. It clearly indicates that the method developed here can be employed to investigate the high temperature behaviour, particularly the phase transformations on heating and cooling, of metallurgical slags as a function of composition, temperature and time. The existence of a solid dicalcium silicate (C_2S) phase was detected in BOS-type slag at steelmaking temperatures of up to 1650 °C. The slag phases during heating and cooling varied with the slag compositions, and the difference in slag phases has been found between the neutron diffraction detection and thermodynamic package prediction.

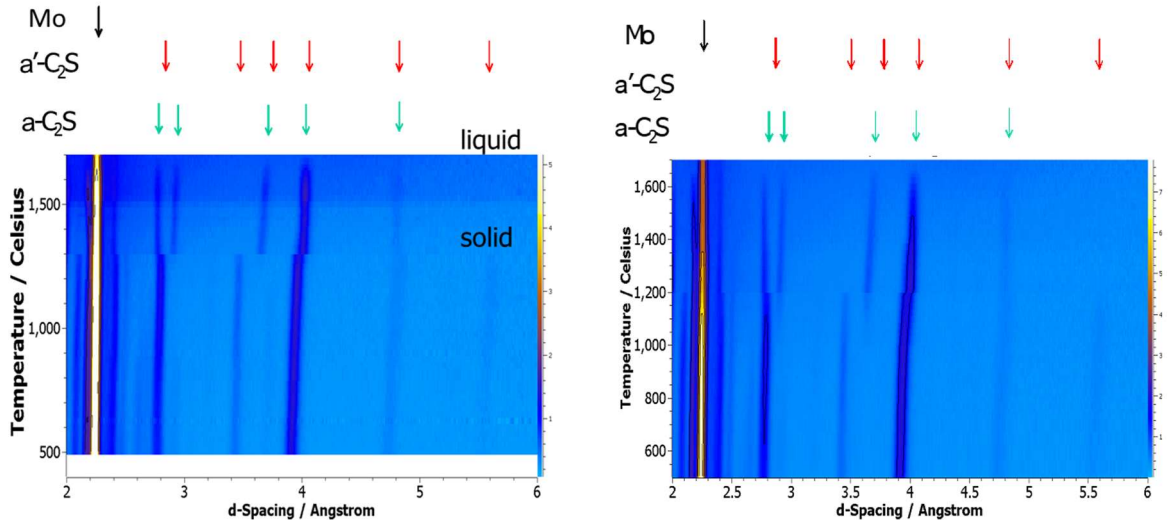

Fig. 2 Phase evolution of a synthetic BOS slag (CaO-SiO_2-FeO-MnO-Al_2O_3-MgO, CaO/SiO_2=2.5, and FeO=20 mass%) during heating (left) and cooling (right).

IV. TRANSITION PHENOMENA IN BOS SLAGS

The high productivity of the BOS process may be attributed to the reaction between the slag and large volume fraction of metal droplets dispersed in the slag forming a slag/metal emulsion. The reaction mechanisms between these two phases have not been well understood. A combination of high temperature confocal laser scanning microscopy (HT-CLSM), micro X-ray computed tomography (micro-XCT), and phase-field modeling has been used to clearly reveal the reaction mechanisms between BOS-type slag and steel droplets in relation to its refining behavior [3]. Fig. 3 illustrates the micro-XCT images (only the metal proportion shown) of fast-quenched Fe-BOS type slag samples obtained on HT-CLSM at 1873 K as a function of reaction time. The Fe droplet used was Fe-O (34 ppm)

and the slag was CaO-SiO_2-FeO-MgO-P_2O_5 (CaO/SiO_2=2.3, FeO=32 mass %) system. It has been clearly observed the progress of emulsification from a single molten sphere droplet at 0 second, through partial emulsification at 25 seconds due to drastically increased perturbation, to full emulsification of metal droplets in the slag at 65 seconds. This spontaneous emulsification is caused by the fast material exchange (i.e. oxygen exchange) between the BOS type slag and Fe droplet, which is successfully simulated by phase-field modelling.

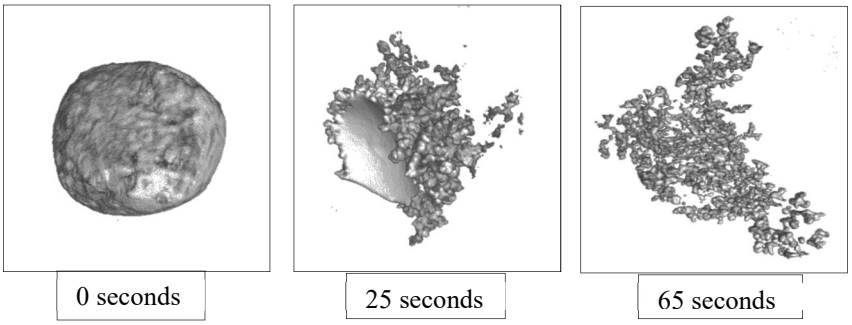

Fig. 3 Micro-XCT images of the Fe droplet (grey) – slag (not shown) system against reaction time.

V. A NOVEL PROCESS TO RECOVER ENERGY AND MATERIALS IN BOS SLAG

A novel process was developed [4, 5] to recover thermal energy in molten BOS slag as syngas and iron oxide in the form of magnetite by controlling crystallization of the BOS slag after reacting molten BOS slag with moisture. This process is based on the reaction of the molten steelmaking slag with the moist atmosphere. In addition to thermodynamic simulation, the process was fundamentally verified by online measuring H_2 production, determining the conversion from Fe^{2+} to Fe^{3+} via titration analysis and quantitating the magnetite Fe_3O_4 amounts for the slags with different basicities and FeO concentrations. Both the amount of magnetite (Fe_3O_4) in the slag after reacting with moisture and the amount of H_2 gas generated increase with increasing FeO content in the slags studied. However, the amount of magnetite (Fe_3O_4) in the reacted slag and the amount of H_2 gas produced increase with increasing the slag basicity (CaO/SiO_2) up to 1.5, and then decrease accordingly.

VI. CONCLUDING REMARKS

Since its commercialisation in 1950s, the basic oxygen steelmaking (BOS) process has been rapidly established as a dominant process in global crude steel production. BOS slag, a product of hot metal element (Si, Mn, Fe) oxidation and lime/dolomite dissolution, is of great importance to the production of high quality crude steel at low costs as the old adage “Look after the slag and the metal will look after itself” is very appropriate. However, the behaviour of BOS slag inside the BOS vessel (formation and reaction) is still not clear and its recycling has always been challenging. In the past decade, the authors have been continuously endeavouring on improving fundamental understanding of BOS slags, with some researches summarised in this paper. Further research is being carried out.

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